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(54) **Oxychlorination of alkanes to monochlorinated olefins**

(57) A process for the production of a monochlorinated olefin comprises bringing into reaction at an elevated temperature a gaseous mixture

comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising compounds of copper, manganese and titanium, and is useful for the production of vinyl chloride from ethane.

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SPECIFICATION

Production of monochlorinated compounds

The present process relates to the production of monochlorinated compounds by the oxychlorination of alkanes.

5 Vinyl chloride is at present manufactured in an essentially two stage process by the oxychlorination of ethylene. Since ethane is potentially a much cheaper feedstock there is considerable incentive to devise a suitable alternative process, particularly if a single stage process can be developed. 5

Several possible processes have been disclosed (e.g. US 3,937,744; Ger Off 2,540,067; US 3,629,351 and GB 2009164). In general these employ similar catalysts to those employed for ethylene oxychlorination, but it is generally found that much higher reaction temperatures are required (450—700°C as compared with about 350°—500°C). This is a serious disadvantage since the catalyst can be molten or partially volatile (necessitating a complex reactor design) and the highly corrosive reaction conditions require the use of expensive construction materials. 10

We have now discovered certain catalysts which can operate in a temperature region substantially below that hitherto possible and thus reduce corrosion/erosion problems. The catalysts may be used in the solid particulate state, thus avoiding reactor problems associated with molten salts and permitting the use of both fixed and fluid bed reactors. These catalysts thus afford the advantage of a selective single stage process based on ethane feedstock. 15

According to the present invention, we provide a process for the production of a monochlorinated olefin which comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising compounds of copper, manganese and titanium. 20

The catalyst composition may include one or more additional components, for example, cerium, thorium, iron or zinc compounds.

25 The process of the invention is applicable to a range of alkane starting materials, especially alkanes having 2 to 4 carbon atoms, for example ethane. The starting material may comprise an alkane/alkene mixture. The alkene may be, for example, ethylene, propylene and various butenes. 25

The process of the invention is especially applicable to the production of vinyl chloride from ethane or ethane/ethylene mixture. Suitable catalyst compositions include those in which the atomic ratio of copper:manganese:titanium is in the range 1:0.1:1 to 1:10:25. Particularly valuable results are obtained when this ratio is substantially 1:1:10. 30

When additional components are present, the atomic ratio of each additional metal relative to the copper present is suitably within the range 0.1 to 5. Particularly valuable results have been obtained when the atomic ratio Cu:Mn:X:Y:Ti is substantially 1:1:0.5:0.5:10, the metals X and Y being selected from Ce, Th, Fe and Zn. 35

The catalyst may conveniently be prepared by coprecipitation of the appropriate oxides, which coprecipitation may be effected chemically, thermally or electrically, or by a combination of these methods. Suitably, the coprecipitation comprises preparing a solution containing the materials from which the desired components can be precipitated. Alternatively, the catalysts may be prepared by sintering the components or by combining the molten components. Under reaction conditions, the oxides may be converted partly or wholly to the corresponding chlorides and/or oxychlorides. 40

The catalyst may be supported if desired on known carriers such as, for example, silica, alumina, titania or silicon carbide. The surface area of the support can be varied widely but is usually in the range 0.1 to 50 m²/g. 45

The supported catalyst may be employed in fixed, moving or fluidised beds of the appropriate size. The reaction temperature may vary according to the reactant employed. Suitably, for example for the oxychlorination of ethane or ethane/ethylene, the reaction temperatures are in the range 250°C—500°C, for example 300°C—475°C. The reaction is normally carried out under atmospheric or superatmospheric pressure, e.g. at a pressure in the range 1 to 100 bars. 50

The source of oxygen may be oxygen itself or oxygen enriched air. The molar ratios of alkane or alkane/alkene mixture and oxygen are preferably in the range 0.1 to 10 moles of oxygen for each mole of alkane or alkane-alkene mixture, for example 0.5 to 2 moles of oxygen for each mole of alkane or alkane/alkene mixture. 55

The source of chlorine is suitably hydrogen chloride or a mixture of chlorine itself and hydrogen chloride, or a mixture of hydrogen chloride and/or chlorine and chlorinated hydrocarbons (e.g. chlorohydrocarbons such as ethyl chloride, ethylene dichloride). It is preferred to use hydrogen chloride or a mixture of chlorine and hydrogen chloride (including ammonium chloride which on heating decomposes to give hydrogen chloride). Typically, the reaction mixture contains 0.1 to 10 moles of hydrogen chloride, for example 1 to 3 moles of hydrogen chloride for each mole of alkane or alkane/alkene mixture. 60

The products of the reaction may be isolated and used as such or, if desired, may be recycled wholly or partially to the reactor in order to increase the yield of monochlorinated olefin, e.g. vinyl chloride.

The invention is illustrated by the following Examples.

EXAMPLE 1

A Cu/Mn/Ti catalyst was prepared as follows: to 170 ml of a 15% solution of titanium tetrachloride was added an equal volume of water, followed by ammonium hydroxide until the pH of the solution was greater than 7.0. The resulting precipitate was filtered and washed until free from chloride. To this precipitate was added a mixture of 6.5 ml of a 50% solution of $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and 3.62 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ dissolved in 40 ml of water. The resulting mixture was evaporated to dryness, heated at 120°C for 16 hours and finally calcined at 500°C for 16 hours.

After grinding to 250—500 μm mesh size, the catalyst was loaded into a $\frac{1}{2}$ " O.D. tubular micro reactor (equipped with an on-line G.L.C. system) to give a bed length of 5 cm or 10 cm. The catalyst was pretreated in a current of HCl for 1 hour at 400°C followed by N_2 for 15 minutes at 250°C. Catalytic performance was then evaluated under a range of gas feed conditions and over a range of temperatures. The products were analysed using on-line G.L.C. The results obtained are shown in Table 1.

The catalyst used in this Example had a Cu:Mn:Ti atomic ratio of 1:1:10.

EXAMPLE 2

A Cu/Mn/Ti catalyst was prepared and tested as in Example 1 but with an atomic ratio of 1:1:15. The results given in Table 2 were obtained with a feed rate of 25 ml min^{-1} air, 5 ml min^{-1} ethane and 5 ml min^{-1} HCl.

EXAMPLE 3

A Cu/Mn/Ti catalyst having an atomic ratio of 1:4:4 was prepared and tested as in Example 1. Results are summarised in Table 3.

TABLE 1

ml min ⁻¹			Temp. °C.	Conversion %	Selectivity %					
					Air	Ethane	HCl	CO ₂	C ₂ H ₄	VC
25	5	5	400	49.64	14.26	14.53	28.60	0.48	13.56	25.98
25	5	5	425	56.46	9.97	23.58	37.79	0.24	9.34	18.25
25	5	5	450	64.20	6.59	35.55	40.02	0.28	6.36	8.34
25	5	5	475	65.57	7.21	52.94	30.88	0.43	2.80	2.58
25	5	5	500	62.57	9.41	72.05	13.13	0.47	0.68	0.76
REPEAT PREPARATION OF EXAMPLE 1										
25	5	5	350	48.15	11.74	4.94	9.52	2.96	22.62	43.15
25	5	5	400	56.81	6.94	13.65	34.68	0.40	18.03	23.48
25	5	5	425	59.73	6.49	23.35	42.27	0.50	11.98	12.94
25	5	5	450	63.50	6.06	37.54	40.82	0.72	6.87	5.72
25	5	5	475	65.41	6.65	54.36	30.74	0.87	2.95	1.91
25	5	5	500	64.26	8.08	74.17	13.94	0.82	0	0

TABLE 2

Temp. °C	Conversion %	Selectivity %					
		CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.
400	50.2	6.0	1.4	0.5	20.9	2.9	1.7
450	77.4	6.0	13.5	19.4	0.1	11.1	6.6
475	83.3	5.6	28.0	29.9	2.5	8.1	4.7
500	86.5	6.6	49.5	29.5	0.2	4.6	2.8
						E.D.C.	β Tri
						63.1	—
						40.8	2.3
						19.3	—
						4.8	—

TABLE 3

Temp. °C	Conversion %	Selectivity %					
		CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.
400	44	16	3.3	1.7	7.2	9.4	6.1
425	61.8	12.0	8.5	8.8	0.5	15.5	9.4
450	60.2	17.3	18.8	25.4	—	14.4	8.5
500	74.1	9.1	44.1	27.2	—	7.6	4.7
						E.D.C.	β Tri
						48.8	2.3
						36.3	1.1
						18.0	—
						4.0	—

EXAMPLE 4

A Cu/Ce/Th/Mn/Ti catalyst was prepared in the following manner: to 85 ml of a 15% solution of TiCl_4 was added 2.038 g of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ dissolved in 30 ml water and a solution of 2.234 g of $\text{Th}(\text{NO}_3)_4 \cdot 6 \text{H}_2\text{O}$ in 55 ml water. To the resulting mixture 50 ml of 25% NH_4OH was added to give a pale yellow precipitate which was filtered and washed with water until the washings were no longer alkaline. A mixture of 1.819 g $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ in 40 ml of water and 3.2 ml of a 50% solution of $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was added to the yellow precipitate and allowed to stand for 16 hours. The mixture was then evaporated to dryness and heated overnight at 120°C . The temperature of the furnace was gradually increased to 500°C , after which the catalyst was calcined for 16 hours at 500°C . The catalytic performance was then evaluated in a microreactor as in Example 1 and the results obtained are shown in Table 4.

The catalyst used in this Example had a Cu:Ce:Th:Mn:Ti atomic ratio of 1:0.5:0.5:1:10.

EXAMPLE 5

A Cu/Me/Fe/Ti catalyst was made in the following manner: a solution of 85 ml of 15% TiCl_4 was mixed with 3.03 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ dissolved in 10 ml water and the resulting mixture diluted with an equal volume of water. A 25% solution of NH_4OH was added (60 ml) to give a yellow-brown precipitate which was then allowed to stand overnight. The precipitate was filtered and washed alkaline-free. To this precipitate was added a mixture of 1.609 g $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ in 40 ml water and 3.2 ml of a 50% solution of $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$. When the addition was complete, the resulting slurry was thoroughly stirred and allowed to stand for 16 hours. The mixture was then evaporated to dryness, dried overnight at 120°C and finally calcined at 500°C for 16 hours. The catalyst was packed into a microreactor and tested as in Example 1. The results obtained are shown in Table 5.

TABLE 4

ml min ⁻¹			Temp. °C	Conversion %	Selectivity %						
					Air	Ethane	HCl	CO ₂	C ₂ H ₄	VC	EC
25	5	5	350	26.45	6.35	1.07	0.28	15.31	2.38	1.28	72.44
25	5	5	400	56.62	14.14	17.76	23.97	0	10.59	5.11	26.45
25	5	5	425	71.17	12.73	24.72	33.08	0	10.19	5.02	12.54
25	5	5	400	82.79	7.95	35.31	31.99	0	13.73	4.68	4.77
12.5	2.5	2.5	400	48.16	19.05	12.34	27.17	0	10.88	5.62	22.92
12.5	2.5	2.5	425	58.40	15.11	18.56	36.99	0	10.21	5.23	12.34
12.5	2.5	2.5	425	62.61	12.65	13.92	37.43	0	13.65	7.01	13.61
12.5	2.5	5.0	425	67.76	3.61	8.33	34.58	0	20.98	11.20	19.19
12.5	2.5	6.0	425	36.67	1.82	36.71	32.42	0.21	6.87	3.11	18.39

TABLE 5

ml min ⁻¹			Temp. °C	Conversion %	Selectivity %						
					Air	Ethane	HCl	CO ₂	C ₂ H ₄	VC	EC
25	5	5	350	27.50	10.15	0.97	0.25	17.64	1.66	0.88	64.91
25	5	5	400	53.17	24.22	18.77	16.22	0.08	9.95	5.97	21.52
25	5	5	450	58.33	17.56	28.62	31.44	0.08	8.45	5.23	6.08
25	5	5	500	79.35	8.53	52.63	29.12	0.26	4.93	2.90	0.15

The catalyst used in this Example had a Cu:Mn:Fe:Ti atomic ratio of 1:1:1:10.

EXAMPLE 6

A Cu/Mn/Zn/Ti catalyst was prepared as follows: a solution of 3.718 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in 100 ml of water was mixed with 113 ml of a 50% solution of TiCl_4 . The solution was made ammoniacal by the addition of NH_4OH and the resulting precipitate filtered and washed until alkali-free. To the washed precipitate was added a mixture of 3.02 g $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ in 35 ml water and 5.3 ml of 50% $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$. The mixture was evaporated to dryness, dried for 16 hours at 120°C and finally calcined at 500°C for 16 hours. The catalyst was packed into a microreactor and its catalytic performance evaluated as in Example 1 and the results obtained are shown in Table 6.

The catalyst used in this Example had a Cu:Mn:Zn:Ti atomic ratio of 1:1:1:8.

Notes on Tables 1—7

- VC = vinyl chloride
- EC = ethyl chloride
- Cis D.C.E. = cis dichloroethylene
- 15 Trans D.C.E. = trans dichloroethylene 15
- EDC = ethylene dichloride
- β Tri = β -trichloroethane

TABLE 6

ml min ⁻¹ .			Temp. °C	Conversion %	Selectivity %						
Air	Ethane	HCl			CO ₂	C ₂ H ₄	VC	EC	Cls D.C.E.	Trans D.C.E.	E.D.C.
25	5	5	400	43.02	16.22	3.78	15.62	0.22	23.66	15.05	19.95
25	5	5	425	53.32	17.78	9.95	34.22	0	15.99	9.31	8.00
25	5	5	450	57.29	16.13	19.48	38.35	0.15	13.50	7.88	1.36
25	5	5	475	63.70	12.37	33.29	34.04	0.13	10.29	6.07	0.17
25	5	5	500	73.95	8.85	49.36	27.07	0.03	7.24	4.30	0

EXAMPLE 7

A range of compositions of Cu/Mn/Zn/Ti catalysts were prepared and evaluated as in Example 6. The results of reaction at 450°C are summarised in Table 7.

TABLE 7

Catalyst Comp. (atomic)				Temp. %	Conv. %	Selectivity %							
Cu	Mn	Zn	Ti			CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.	E.D.C.	β Tri
1	1	1	1	450	57.6	13.4	1.4	5.5	2.4	15.1	7.4	32.0	7.5
1	1	1	2	450	60.1	12.9	14.6	31.9	—	14.3	7.0	15.1	—
1	1	1	6	450	53.6	18.4	36.5	36.5	—	14.4	8.1	1.2	—
1	1	1	9	450	62.4	13.5	19.9	40.0	0.1	12.5	7.0	4.0	—
1	1	2	25	450	49.0	14.9	6.4	15.9	0.1	26.4	16.0	4.4	—
1	1	2	10	450	82.7	25.4	5.4	16.6	—	22.2	14.1	1.3	5.4
1	2	1	8	450	67.2	21.1	6.7	27.1	—	14.8	10.6	12.2	—

CLAIMS

1. A process for the production of a monochlorinated olefin which comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising compounds of copper, manganese and titanium. 5
2. A process according to claim 1 wherein the catalyst composition also includes one or more compounds of cerium, thorium, iron or zinc.
3. A process according to claim 1 or claim 2 wherein the alkane is ethane.
4. A process according to any one of the preceding claims wherein the catalyst composition is such that the atomic ratio of copper:manganese:titanium is in the range 1:0.1:1 to 1:10:25. 10
5. A process according to claim 4 wherein the atomic ratio of copper:manganese:titanium is substantially 1:1:10.
6. A process according to any one of the preceding claims wherein the gaseous mixture contains from 0.1 to 10 moles of oxygen for each mole of alkane.
7. A process according to claim 6 wherein the gaseous mixture contains from 0.5 to 2 moles of oxygen for each mole of alkane. 15
8. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing Examples.